

Process for the preparation of a coating, a coated substrate, an adhesive, film or sheet.

The invention relates to a process for the preparation of a coating, coated substrate, adhesive, film or sheet, to the thus obtained product and to the coating mixture to be used in the process.

5 In the course of years several methods have been developed for solvent-free application of polyurethanes in the preparation of coatings, films and the like. An overview of these methods is presented in WO-123451. In this patent application an invention is described which
10 caused a breakthrough in the development of high solid systems. This invention describes a process for the preparation of coatings in which a mixture of a polyisocyanate-, polyepoxide-, polyanhydride-, or polyketone- functional compound and a compound containing
15 a reactive hydrogen, which mixture is not reactive at room temperature, is applied onto a substrate, whereafter the mixture reacts at elevated temperatures from 30-300°C. The compound containing a reactive hydrogen is a solid, which may be present in the mixture as a fine powder or as a
20 dispersion in a medium.

Another new method in the field of developing high solid content systems is described in the Dutch patent application no 1018797. It relates to a combination of the system described above and another reactive system.
25 A problem of these known systems is that for certain applications a lower reaction temperature is required, while in addition the pot-life of the coating mixture must be sufficiently long. An example of this is the application to temperature-sensitive substrates, such as
30 leather. Other applications have the disadvantage that a higher reaction temperature is required. An example is the application in a two- step reaction in which an early start of the second reaction- step has to be prevented.

EP-171015 describes a method of delaying the

reactions between polyisocyanate and aromatic diamines or, at ambient temperature, solid aliphatic diamines by surrounding the same with a polymer layer, in particular with a polyurethane layer, which melts when the 5 temperature is elevated, whereafter the diamine can react. A disadvantage of this invention is that it does not relate to hydrazides, which are known to yield strong films and to be anti-yellowing. Moreover the reaction time is from 1-2 hrs to possibly 1-2 days, also at higher 10 temperatures, which is much too long in the coating industry. In addition, the considerable disadvantage of the polyurethane films which are formed by using aromatic diamines is that they yellow easily and the diamines themselves are mutagenic and/or carcinogenic.

15 The object of the present invention is to provide a process in which the disadvantages mentioned are eliminated effectively.

According to the present invention there is provided a process for the preparation of a coating, 20 coated substrate, adhesive, film, sheet and the like, in which process a coating mixture which comprises a reactive system of a polyisocyanate-functional, polyketone-functional, polyepoxide-functional, polyanhydride-functional and/or polycyclic carbonate-functional compound 25 or polymer and a dispersion or fine powder of a compound containing a reactive hydrogen, which mixture is not or low-reactive at room temperature, is applied onto a substrate, resulting in a substrate coated with the coating mixture, followed by reacting the compounds 30 mentioned above by elevating the temperature, characterized, in that the reaction temperature and consequently the reaction rate can be adjusted as desired by the addition of an additive to the coating mixture, or to one of the reactants of the coating mixture prior to 35 the mixing with the other component, and in which optionally another reactive system is present and both systems are essentially reacted as a sequential two step reaction while between these reaction steps the coating is

remoulded. Such a remoulding may be the application of a grain or a fold.

Preferably the compound containing the reactive hydrogen is a compound which is crystalline at a 5 temperature below 30°C. At grinding the compound or dispersing it in a non-reactive material it maintains its crystalline form.

Preferably the compound containing reactive hydrogen is a polyhydrazide and/or polysemicarbazide 10 and/or piperazine, while, most preferably, the compound is adipic dihydrazide and/or carbodihydrazide. Preferably these compounds are present as a dispersion in a non-reactive material as described in WO-123451.

Usually the additive is water, acid, base, a 15 metal catalyst, a solvent, a polyisocyanate-functional compound, a polyketone-functional compound, a melamine and/or a surfactant.

Surprisingly it appeared that several factors are of importance in the adjustment of the reaction such as, 20 the concentration of the additive, the sequence of the addition of the additives, the separate addition of the additives to one of the reactants of the coating mixture prior to mixing of these reactants, the equilibration time of the additives in the coating mixture or in one of the 25 reactants of the coating mixture.

In particular it appeared that the reaction rate is increased by the addition of water, a polar non-protic organic solvent, an acid, a base, a metal catalyst, and/or a surfactant to the coating mixture, and a coating is 30 formed at a temperature which is 3-50°C below the original reaction temperature; which is the conventional temperature which is needed for the formation of the coating. A great advantage of this adjustment of the process is that the process is now also suitable for 35 temperature-sensitive substrates, such as leather. A second advantage is that at lower temperatures the energy costs for preparing a coating are lower.

Surprisingly it appeared that the reaction is delayed when 0.0001-10% by weight of water and/or acid

and/or an amine, polyamine, alcohol or polyol is not added to the coating mixture, but first to a dispersion of the compound containing the reactive hydrogen, prior to mixing it with a polyisocyanate-functional compound, and a 5 coating is formed at a temperature that is 3-50°C higher than the original reaction temperature. An explanation for this is that when the water- and/or acid-, amine-, polyamine-, alcohol-, or polyol-containing dispersion is mixed with a polyisocyanate-functional compound, the 10 compound containing a reactive hydrogen is preferably surrounded by a thin layer of the water and/or acid, amine, polyamine, alcohol or polyol, because of the strong polar or hygroscopic character of the particles. A part of the compound containing a reactive hydrogen dissolves in 15 this thin layer and reacts immediately with the polyisocyanate, the moment that it makes contact with the polyisocyanate. As a consequence a thin ureum- or urethane- oligomer layer is formed surrounding the rest of the particle, which is a barrier for the rest of the 20 polyisocyanate. In the case that an amine, polyamine, alcohol or polyol is present in the dispersion, these compounds also react completely or partially with the polyisocyanate and contribute to the formation of the thin barrier layer. At increasing the temperature the barrier 25 is broken and the rest of the polyisocyanate-functional compound and the rest of the compound containing a reactive hydrogen react further. The part of the compound containing a reactive hydrogen which is dissolved does react at room temperature, because this is mono-molecular 30 material and is not fixed in the crystalline form.

The addition of 0.001-0.2 equivalents of a polyisocyanate-functional compound, such as 1,6-hexanediiisocyanate, toluenediiisocyanate, 4,4'-diisocyanatocyclohexylmethane, 4,4'-diisocyanatophenylmethane, 3-isocyanatomethyl-3,5,5,-trimethylcyclohexyl-isocyanate, tetramethylxylenediisocyanate, a (triisocyanatoalkyl- or cycloalkyl)-isocyanurate, a (diisocyanato-alkyl- or cycloalkyl)uretdion, or an isocyanate-functional polyurethane based on the mentioned

diisocyanates, and/or an aliphatic or aromatic polycarbodiimide and/or an organic solvent, to a dispersion of the compound containing a reactive hydrogen, prior to the mixing with the polyisocyanate-functional compound also delays the reaction and a coating is formed at a temperature that is 3-50°C higher than the original reaction temperature.

According to the process the reaction is also delayed by the addition of 0.001-0.2 equivalent of one of the polyisocyanate-functional compounds with a low molecular weight described above, to a polyisocyanate-functional polyurethane, prior to the mixing with the compound containing a reactive hydrogen and a coating is formed at a temperature that is 3-50°C higher than the original reaction temperature.

An explanation for the need to increase the reaction temperature for both cases described above is, that after the addition of 0.002-0.2 equivalents of a polyisocyanate-functional compound, or an aliphatic or aromatic polycarbodiimide, to the dispersion with the compound containing a reactive hydrogen or, after the addition of 0.001-0.2 equivalent of one of the mentioned low-molecular polyisocyanate-functional compounds to an isocyanate-functional polyurethane, the polyisocyanate-functional compound, respectively the polycarbodiimide reacts with the borderline molecules of the particle with the reactive hydrogen and a thin ureum- or urethane-oligomer layer, respectively an acylureum-oligomer layer is formed around the rest of the particle, which forms a barrier for the rest of the polyisocyanate. At increasing the temperature the barrier is broken and the rest of the polyisocyanate-functional compound and the rest of the compound containing a reactive hydrogen react.

In EP-171015 a comparable process is used with aromatic diamines and solid aliphatic polyamines which are surrounded by a polyurethane layer. However, the polyhydrazides and semicarbazides and carbodihydrazide, which are applied in the present invention, have unique properties compared to the polyamines mentioned,

especially when they are applied in a solid form. The main reason for this is that, because of the morphological properties of the polyhydrazides, polysemicarbazides and carbodihydrazide, they are completely inert at room

5 temperature and even at temperatures up to and above 50°C they are often inert in both, reactive and non-reactive, media. In conventional applications they are used as chain extender or as crosslinker in the preparation of polyurethanes, just like aliphatic or aromatic polyamines.

10 They have a reactivity comparable to that of the aliphatic polyamines when they are dissolved in water or in an organic solvent. However, when the polyhydrazides and semicarbazides are in the solid form, the obtained mixtures with a polyisocyanate-functional compound have a

15 long pot-life, and sometimes even an unlimited pot-life, as described in WO-123451, while aliphatic amines, also when they are solid, already react with a polyisocyanate during the mixing with a polyisocyanate and a gel is formed immediately. When in a comparable way as in EP-

20 171015 and according to the description above an aliphatic polyamine is surrounded by a polyurethane layer, and the protected polyamine is mixed with a polyisocyanate, the mixture does reacts within 1 minute. In the first place, this means that the crystal energy of the polyhydrazides,

25 semicarbazides and carbodihydrazide is much higher than that of the aliphatic polyamines. In the second place, it is much more difficult to break the barrier of the oligomer layer in which a polyhydrazide, polysemicarbazide or carbodihydrazide is used, than when an aliphatic amine

30 is used.

Further, it is known that the reactivity of polyhydrazides, polysemicarbazides or carbodihydrazide, when they are dissolved in water or in an organic solvent, is much greater than that of aromatic polyamines towards

35 polyisocyanates. Yet, according to EP-171015 and the references cited therein, the aromatic polyamines in a solid form have to be protected somehow to obtain a sufficient pot-life when mixed with a polyisocyanate. As mentioned before, this is not required for polyhydrazides,

semicarbazides and carbodihydrazide. When applying the protected aromatic polyamines, the reaction mixture with the polyisocyanate is heated for 1 to 2 hrs at 120-140°C, and sometimes even for 1 to 2 days at a temperature of 110 to 120°C to break the barrier layer and to obtain a complete reaction. These reaction times are far too long in the coating industry. A reaction time of 2 to 3 minutes is required at a temperature of 50 to 200°C and preferably at 50 to 160°C. Surprisingly it appeared that in the application of the polyhydrazides, polysemicarbazides and carbodihydrazide which have a barrier layer according to the invention, a complete reaction with a polyisocyanate can be obtained in the same time as with the unprotected material. Usually this time is from 2 to 3 min at 50 to 160°C and depends on the type of polyisocyanate, whether a polyhydrazide, polysemicarbazide or carbodihydrazide is used and on the type of application. The reaction temperature of the reaction mixtures, in which the polyhydrazide, polysemicarbazide or carbodihydrazide is protected by a barrier layer, may be higher than in the absence of such a layer, but the reaction is immediate and complete.

The use of polyhydrazides, polysemicarbazides and carbodihydrazide is advantageous for several reasons, both in the protected form as well as in the pure form. In the first place, in the reaction with polyisocyanates very strong, resistant and non-yellowing films are obtained. Unlike aliphatic or aromatic polyamines these compounds do not have a penetrating smell and they are not corrosive. An important advantage, particularly with respect to aromatic polyamines, is that the polyhydrazides, polysemicarbazides or carbodihydrazide are not mutagenic and/or carcinogenic.

According to the process the reaction is further delayed by the addition of 0.001 to 0.20 equivalents of an aldehyde-, polyaldehyde-, ketone- and/or polyketone-functional compound to a dispersion of the compound containing a reactive hydrogen, prior to mixing with a polyisocyanate-functional compound, and a coating is

formed at an reaction temperature which is 3-50°C higher than the original reaction temperature.

In an analogous way as with the addition of polyisocyanates a barrier is formed, which in this case is 5 a polyimine layer or a polyhydrazone layer. The ketone functional compound which is used as additive is preferably a dialkyl ketone, a cycloalkyl ketone, an alkanal, a polyketone-alkane, -cycloalkane or -aromatic, or a ketone-functional polymer with ketone functions in 10 the main chain or in the side chain, such as a ketone-functional polyesterdiol, polyacrylate or polyurethane.

Many of the coating mixtures of the polyhydrazide or polysemicarbazide with a polyisocyanate have a pot-life of at least 3 weeks. However, the pot-life of some of them 15 is shorter, in particular when carbodihydrazide is used as the compound containing a reactive hydrogen. A second effect of the addition of water and/or acid, an amine, a polyamine, an alcohol, a polyol, or of the addition of 0.002 to 0.20 equivalents of a polyisocyanate-functional 20 compound to a dispersion containing a reactive hydrogen, prior to mixing with the polyisocyanate functional compound, or of 0.001-0.20 equivalent of a polyketone-functional compound, or of 0.002-0.2 equivalent of a low molecular polyisocyanate-functional compound to a 25 isocyanate-functional polyurethane, is that the pot-life of the coating mixture is increased from 5-240 min up to at least 1 day and preferably to at least 14 days.

As mentioned before, there is possible a second reactive system present. It comprises on the one hand a 30 ketone, anhydride, epoxide, a polyisocyanate with a different reactivity, a blocked isocyanate and/or a cyclic carbonate function, or the compound with the isocyanate functionality, and on the other hand a hydrazide or semicarbazide with a lower reactivity or with a different 35 particle size, an amine, a hindered amine, chlorinated amine, a polymer protected amine, a blocked amine, azetidine, aspartate, carboxyl, aromatic amine, hydroxide and/or melamine function, and/or the other reactive system comprises polysiloxane or melamine functions, which are

polymerisable by self-condensation, and/or the other reactive system comprises an unsaturated compound which undergoes an addition polymerisation, in which the reactive groups from the second reactive system may be 5 coupled to the compound containing the reactive hydrogen, or to the polyisocyanate-functional, a polyketone-functional, a polyepoxide functional, a polyanhydride functional, and/or a polycarbonate-functional compound or polymer of the first reactive system or to another 10 compound.

According to the invention it is possible that the second reactive system reacts faster than the first reactive system in the presence of the mentioned additives.

15 Another option is that the reaction of the second reactive system is slower than that of the first reactive system in the presence of the mentioned additives.

In WO 0123451 an overview is presented of the isocyanate-functional and/or ketone-functional and/or 20 epoxide-functional, and/or anhydride-functional compounds which may be used in the invention and of the ways that the coating mixtures may be applied. Naturally, the compounds may contain non-reactive groups such as allophenate groups, biurete groups, isocyanurate groups, 25 and reactive groups such as carbodiimide groups or unsaturated groups.

The invention further extends to the product obtained by the process, such as a coating, coated substrate, film or sheet.

30 The present invention is further illustrated by the following examples to which the invention is however not limited. It goes without saying that numerous other embodiments are possible, all within the scope of protection.

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Examples

The following abbreviations and commercial names will be used in the examples:

HDI : 1,6-hexanediisocyanate

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	TDI	:	2,4-toluenediisocyanate or 2,6-toluenediisocyanate or mixtures of these isomers
5	IPDI	:	3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate
	Des W	:	4,4'-diisocyanatocyclohexylmethane
	N-3300	:	Desmodur N-3300; a trisocyanurate based on HDI from Bayer
10	ADH	:	adipic dihydrazide
	CDH	:	carbodihydrazide
	Triton X-100	:	non-ionic emulsifier obtainable from Union Carbide
	Marlipal O 13/120	:	non-ionic emulsifier obtainable from Condea
15	Aerosol OT 100	:	anionic emulsifier obtainable from Cytec
	Synperonic	:	Synperonic PE-L62/LF; a block polymer of ethylene- and propyleneglycol obtainable from PUK.
20	Bisoflex TOT	:	a polyester obtainable from Laporte
	PEC-205	:	a polyketonediol obtainable from Neoresins
	NMP	:	N-methylpyrrolidinone
	MEK	:	methyl ethyl ketone (butanone)
25	EtOAc	:	ethyl acetate
	DMM	:	dimethyl ether of dipropyleneglycol
	EAP	:	ethyl-acid phosphate
	DABCO	:	diaminobicyclo-octanoate
	DBTL	:	dibutyltin laureate
30	SA	:	stoichiometric amount

Example 1: Preparation of an aliphatic isocyanate-functional polyurethane polymer.

Under a nitrogen atmosphere 126.5. g (752.98 mmol) of HDI was added at 60-70°C to a mixture of 358.49 g (400 mmol) of polypropylene glycol with a molecular weight of 1007, 5.0 g (37.31 mmol) of trimethylolpropane and 10.0 g (96.0 mmol) of 2,2-dimethyl-1,3-propanediol while stirring. The mixture was heated to 90°C and was reacted

for two hours at this temperature, forming an isocyanate-functional polyurethane. After 1 hr of reaction time 0.1 g of tinoctoate was added as a catalyst. The reaction mixture was cooled down. The remaining NCO-content was 5 measured and was 3.98% by weight.

Example 2: Preparation of an aromatic isocyanate-functional polyurethane.

The procedure of Example 1 was repeated, with the 10 exception that an isocyanate-functional polyurethane was prepared from 129.2 g (742.53 mmol) of TDI, 658.76 g (658.76 mmol) of polypropylene glycol with a molecular weight of 2000 and 12.0 g (89.55 mmol) of trimethylolpropane. The reaction temperature was 85°C. The 15 remaining NCO-content was measured and was 2.57% by weight.

Example 3: Preparation of an aliphatic isocyanate-functional polyurethane.

The procedure of Example 1 was repeated, with the 20 exception that an isocyanate-functional polyurethane was prepared from 112.78 g (507.56 mmol) of IPDI, 139.21 g (138.24 mmol) of polypropylene glycol with a molecular weight of 1007, 163.77 g (81.89 mmol) of polypropylene 25 glycol with a molecular weight of 2000 and 4.2 g (31.34 mmol) of trimethylolpropane. The reaction temperature was 100°C. The remaining NCO-content was measured and was 4.43% by weight.

30 Example 4: Preparation of an isocyanate-functional polyurethane containing incorporated unsaturated groups.

Under a nitrogen atmosphere 4.55 g of a hydroxy-polyesteracrylate (obtainable as Tone M-100 from Union 35 Carbide) and 0.02 g of dibutyltindilaureate were added to 120 g of the product of Example 3 while stirring. The mixture was stirred for 1.5 hr at 90°C and cooled down. The remaining NCO-content was 3.40%. Just before testing the product in Example 12, 0.4 g of an UV-initiator (CGI-

1800 van Ciba) in 4 g of dipropylene glycol-dimethylether was stirred into 50 g of the product.

5 Example 5 : Evaluation of the effect of the addition of water or N-methylpyrrolidinone to a coating mixture on the reaction temperature needed for the formation of a polyurethane coating

10 The isocyanate-functional polyurethane of Example 1, 2 or 3 was mixed with a, with respect to the NCO-content, equivalent amount of a 4:6 (w/w) dispersion of carbodihydrazide or adipic dihydrazide in Bisoflex TOT. Beforehand an amount of water or NMP was mixed into the isocyanate-functional polyurethane. 500 μ m of the obtained mixture was spread onto a pre-heated plate. The 15 temperature was raised serially with 5°C (\pm 1°C) at a time. After 3 min the progress of the reaction was checked. The lowest temperature required to obtain a dry and flexible film was measured. The results are presented in Table A.

Table A: Effect of water or NMP on the coating formation using an isocyanate-functional polyurethane and a carbodihydrazide dispersion or an adipic dihydrazide dispersion.

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Poly-urethane	Added to the polyurethane (weight %)	compound containing reactive hydrogen	minimal temperature complete curing within 3 min (°C)	pot-life ^{a)} at 20°C (min)
Example 1	-	CDH	90	>6000
	0.5% water	CDH	80	40
	1.0% water	CDH	80	9
	3.0% water	CDH	70	3
	2.0% NMP	CDH	90	20-40
	5.0% NMP	CDH	80	20-40
	20% NMP	CDH	70	5
	5.0% isohexane	CDH	90	>200
	20% isohexane	CDH	90	>200
	2.0% EtOAc	CDH	90	>200
	5.0% EtOAc	CDH	85	>120
	20% EtOAc	CDH	80	25
	5.0% toluene	CDH	85	>180
	20% toluene	CDH	85	50
	5.0% MEK	CDH	85	>180
	20% MEK	CDH	80	30
	5.0% DMM	CDH	85	>60
	20% DMM	CDH	85	30
	-	ADH	120	>6000
	1% water	ADH	120	300
	3% water	ADH	120	90
Example 2	-	CDH	95	>6000
	1.0% water	CDH	80	10
	3.0% water	CDH	75	0.7
	5.0% water	CDH	70	<0.3
Example 3	-	CDH	90	120
	1.0% water	CDH	85	12
	3.0% water	CDH	80	<3
	5.0% water	CDH	80	<3
	5.0% NMP	CDH	95	30
	-	ADH	125	>6000
	1.0% water	ADH	120	30-60
	3.0% water	ADH	120	30-60

Remarks relating to Table A:

a) pot-life of the coating mixture

10 The results show that

- by the addition of water to an isocyanate-functional polyurethane the minimal reaction temperature for the formation of a coating can be decreased. The effect is

stronger with a HDI-based polymer or TDI-based polymer than with a IPDI-based polymer and the effect is also stronger with a higher percentage of water.

- the pot-life of the coating mixture is shorter when 5 water is added to the isocyanate-functional polyurethane.
- the addition of solvents has a marginal effect on the reaction temperature; a lower reaction temperature can only be reached by the addition of a larger amount of 10 NMP.
- the pot-life drastically decreases by the addition of solvents, in particular in larger amounts.
- the effects with CDH are more explicit than with ADH.

15 Example 6: Evaluation of the effect of various additives to a coating mixture on the reaction temperature needed for the formation of a polyurethane coating.

The procedure of Example 5 was repeated with 20 several components which were added either to the isocyanate-functional polyurethane, or to the dispersion of carbodihydrazide. Further a dispersion of CDH in the water-soluble Synperonic PE-L62/LF was tested. In this case the isocyanate-functional polyurethane of Example 3 25 was used. The results are presented in Table B.

Table B: Effect of additives on the coating formation using the aliphatic isocyanate-functional polyurethane of Example 3 and a carbodihydrazide dispersion.

Additive added to the CDH-dispersion ^{c)} (weight %)	Additive added to the polyurethane of Example 3	minimal temperature complete curing within 3 min (°C)	pot-life ^{a)} at 20°C (min)
-	-	90	60-90
-	1% water	85	12
-	5% water	80	<3
-	5% NMP	95	~30
1% Marlipal O 13/120	-	90	<2
1% Marlipal O 13/120	5% water	80	<2
5% Marlipal O 13/120	-	90	<3
5% Marlipal O 13/120	5% water	75	<3
1% Aerosol OT 100	-	90	30-40
1% Aerosol OT 100	5% water	80	1
5% Aerosol OT 100	-	95	30-40
5% Aerosol OT 100	5% water	75	1
5% Aerosol OT 100	5% NMP	80	0.8
--	0,1% HDI	95	< 1 ^{d)}
--	0,5% HDI	95	4 ^{d)}
--	1,0% HDI	90	196 ^{d)}
--	1,0% HDI ^{b)}	110	--
--	2,0% HDI	100	196 ^{d)}
--	2,0% HDI ^{b)}	120	--
--	2,0% TDI	120	>288 ^{d)}
--	2,0% IPDI	95	1-3 ^{d)}
--	2,0% Des W	95	1-2 ^{d)}
CDH-dispersion in Synperonic	-	95	40-60
CDH-dispersion in Synperonic	1% water	90	10-15
CDH-dispersion in Synperonic	5% water	85	<2
CDH-dispersion in Synperonic	5% NMP	95	20-30

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Remarks relating to Table B

- a) pot-life of the coating mixture.
- b) Tested after a storage time of the coating mixture of 74 hrs at 50°C.
- c) Dispersion was equilibrated for 24 hrs after the addition of the additive.
- d) pot-life in hrs at 50°C.

The results show that:

- the reaction temperature can be decreased by the addition of a low percentage of water to the polyurethane.
- 5 - the reaction temperature can be increased slightly by the addition of NMP to the polyurethane.
- the reaction temperature can be decreased by the addition of 5% Marlipal O 13/120 or Aerosol OT to the CDH-dispersion and the addition of 5% water to the polyurethane.
- 10 - the reaction temperature can be decreased slightly by the addition of 5% Aerosol OT 100 to the CDH-dispersion and the addition of 5% NMP to the polyurethane.
- the reaction temperature can be increased by the addition of the more reactive polyisocyanates HDI and TDI to the polyurethane. At a higher percentage the effect is stronger. The effect is weaker for the less reactive polyisocyanates IPDI and Des. W.
- 15 - the reaction temperature can be greatly increased by storing the coating mixture with additional HDI at 50°C for 74 hrs.
- when water is added to the polyurethane, the pot-life of the coating mixture will shorten.
- when a more reactive polyisocyanate such as HDI or TDI is added to the polyurethane, the pot-life of the mixture will be greatly extended.
- 20 - the reaction temperature is slightly higher when a water-soluble medium is used for the CDH-dispersion than when Bisoflex TOT is applied.
- 25
- 30

Example 7: Evaluation of the effect on the reaction temperature needed for the formation of a polyurethane coating from the coating mixture after the addition of a surfactant and/or water to a dispersion of a compound containing a reactive hydrogen.

The procedure of Example 5 was repeated, while in this example Triton X-100 and/or water were added to the dispersion of the carbodihydrazide, prior to the

preparation of the coating mixture. In this case the isocyanate-functional polyurethane of Example 3 was used. After the addition of water to the CDH-dispersion the mixture was equilibrated for 24 hrs (which means stored in 5 order to reach an equilibrium) before it was used in the coating mixture. The results are presented in Table C.

Table C: Effect of additives on the coating formation of the aliphatic isocyanate-functional polyurethane of Example 3 and a carbodihydrazide dispersion.

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Triton X-100 in CDH dispersion (weight %)	additive added to the CDH-dispersion (weight %)	minimal temperature complete curing within 3 min (°C)	Pot-life at 50°C ^a (hrs)
0	-	90	<0.8
0	1% water	130	23-47
0	3% water	135	23-96
0	5% water	135	10-16
1	-	90	<1
1	1% water	110	6-22
1	3% water	125	6-22
1	5% water	135	16-20
2	-	90	<0.5
2	1% water	110	3-22
2	3% water	125	47-96
2	5% water	135	46-70
5	-	85	<1
5	1% water	85	<1
5	3% water	115	2-19
5	5% water	125	10-17
5	5% NMP	90	<1

Remarks relating to Table C

a) pot-life of the coating mixture.

The results show that:

15 - the reaction temperature can be increased by the addition of water to the CDH dispersion. The effect is greater when more water is used.

- by the addition of both water and Triton X-100 to the CDH-dispersion opposite effects are found: the reaction temperature will be increased by the addition of more water, while the temperature will be decreased by the addition of more Triton X-100.

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- The pot-life of the coating mixture can be lengthened by the addition of water to the CDH-dispersion. This effect will be less in the presence of more Triton X-100.

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Example 8:

Evaluation of the effect on the reaction temperature needed for the coating mixture to form a polyurethane coating after the addition of polyisocyanates to a dispersion of a compound containing a reactive hydrogen.

The procedure of Example 5 was repeated, while in this case an equivalent short measure of a polyisocyanate was added to the dispersion of CDH or ADH, prior to the preparation of the coating mixture. After the addition of the polyisocyanate to the CDH-dispersion or ADH-dispersion, the mixture was equilibrated for 24 hrs before it was used in the coating mixture. In this case isocyanate-functional polyurethanes of examples 1 and 3 were used. The results are presented in Table D and E.

Table D: Effect of a short measure of polyisocyanates in the ADH-dispersion on the coating formation using the aliphatic isocyanate-functional polyurethane of Example 1 and 3 and an ADH-dispersion.

polyurethane	additive added to the ADH dispersion	minimal temperature complete curing within 3 min (°C)	Pot-life at 50°C between ^{a)} (hrs)
Example 1	-	125	>500
Example 1	0.02 SA HDI	125	>500
Example 1	0.10 SA HDI	130	>500
Example 1	0.02 SA N3300	130	>500
Example 1	0.05 SA N3300	135	>500
Example 3	-	120	>500
Example 3	0.02 SA HDI	135	>500
Example 3	0.10 SA HDI	140	>500
Example 3	0.02 SA N3300	135	>500
Example 3	0.05 SA N3300	145	>500

Table E: Effect of a short measure of polyisocyanates in the CDH-dispersion on the coating formation from the aliphatic isocyanate-functional polyurethane of Example 1 and 3 and a CDH-dispersion.

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polyurethane from Example	additive added to the CDH-dispersion	coating-mixture at 50°C during (hrs)	minimal temperature complete curing within 3 min (°C)	Pot-life at 50°C between ^{a)} (hrs)
Example 1	-	0	85	>384
	0.02 SA HDI	0	110	>384
	0.02 SA IPDI	0	135	>384
	0.02 SA TDI	0	125	>384
Example 3	-	0	90	0-0.8
	0.001 SA HDI	0	95	1-2
	0.001 SA HDI + 0.5% water	0	130	90-120
	0.01 SA HDI	0	100	21-96
	0.01 SA HDI	74	100	
	0.05 SA HDI	0	120	> 864
	0.05 SA HDI	74	120	
	0.10 SA HDI	0	120	> 864
	0.10 SA HDI	72	120	
	0.10 SA product	0	110	168-288
	Example 1			
	0.10 SA product	168	115	
	Example 1			
	0.01 SA TDI	0	120	432-648
	0.01 SA TDI	92	120	
	0.05 SA TDI	0	125	21-92
	0.05 SA TDI	92	120	
	0.01 SA IPDI	0	120	18-93
	0.01 SA IPDI	93	115	
	0.05 SA IPDI	0	125	> 648
	0.05 SA IPDI	93	125	
	0.01 SA Des W	0	125	73-168
	0.01 SA Des W	73	125	
	0.05 SA Des W	0	130	408-624
	0.05 SA Des W	75	130	
	0.01 SA N-3300	0	120	92-168
	0.01 SA N-3300	92	120	
	0.05 SA N-3300	0	125	> 624
	0.05 SA N-3300	92	125	

Remarks relating to Table D and E

a) The pot-life of the coating mixture is the time that the mixture remains liquid

The results show that:

- the reaction temperature can be increased by the addition of a stoichiometric short measure of a polyisocyanate with a low molecular weight or an isocyanate-functional polyurethane to a CDH-dispersion, prior to the preparation of the coating mixture. The strongest effect is found with Des W, followed by IPDI, TDI, HDI and the polyurethane from Example 1.
- the pot-life can be lengthened by the addition of a stoichiometric short measure of polyisocyanate to the CDH-dispersion.
- when the CDH dispersion is protected, the curing temperature of an non-equilibrated coating mixture is comparable to that of a coating mixture which is equilibrated at 50°C.
- the reaction temperature is lower when CDH is used than when ADH is used and the effects of the additives are stronger when CDH is used.

20 Example 9: Evaluation of the effects on the reaction temperature to prepare a polyurethane coating from a coating mixture after the addition of several additives to a dispersion of a compound containing a reactive hydrogen.

25 The procedure of Example 5 was repeated, while in this Example PEC-205 (a polyketonediol), MEK (a ketone), EAP (an acid), DABCO (tertiary amine), isophorondiamine, butanediol, an aromatic or aliphatic polycarbodiimide solution (in Table F presented as aliph-carb en arom-carb) and/or DBTL (a tin compound) was added to the dispersion of the carbodiimide, prior to the preparation of the coating mixture. In several cases water was added as well. The polycarbodiimides were prepared according to EP-507407

30 Example 18 and 32, and the intermediate isocyanate-functional polycarbodiimides were capped with an equivalent amount of n-propanol. After the addition of the additives to the CDH-dispersion the mixtures were equilibrated for 24 hrs at 20°C before they were used in

the coating mixture. When PEC-205 was used the temperature for equilibration was 50°C. The isocyanate-functional polyurethanes of Example 1 and 3 were used. The results are presented in Table F.

Table F: Effect of additives in the CDH-dispersion on the coating formation using the aliphatic isocyanate-functional polymer of Example 3 and a CDH-dispersion.

poly-urethane	Additive added to the CDH-dispersion	minimal temperature complete curing within 3 min (°C)	Pot-life at 50°C between ^{a)} (hrs)
Example 1	-	90	>500
	0.001 SA PEC-205	95	>500
	0.002 SA PEC-205	95	>500
	0.002 SA PEC-205 + 0.5% water	100	>500
	0.002 SA PEC-205 + 0.5% water + 0.15% EAP	125	>500
	1.5% EAP	100	>500
	1.5% DABCO	95	>500
	0.45% DBTL	90	>500
	0.02 SA butanediol	95	>500
	0.02 SA butanediol + 0.5% water	100	>500
	0.02 SA isophorone-diamine	120	>500
	0.02 SA isophorone-diamine + 0.5% water	145	>500
	2% Cymel-303	90	>500
Example 3	-	95	3-4
	0.001 SA PEC-205	100	24-48
	0.002 SA PEC-205	105	24-48
	0.002 SA PEC-205 + 0.5% water	125	24-48
	0.002 SA PEC-205 + 0.5% water + 0.15% EAP	120	24-48
	1% butanone	105	24-48
	1.5% EAP	115	24-48
	1.5% DABCO	95	2-3
	0.45% DBTL	95	2-3
	2% Cymel-303	100	1
	0.005 SA piperazine	105	5-22
	0.02 SA piperazine	105	5-21
	0.10 SA piperazine	110	5-20
	0.5% aliph-carb	105	1-23
	2.0% aliph-carb	110	1-23
	5.0% aliph-carb	115	1-21
	0.5% arom-carb	100	2-18
	2.0% arom-carb	100	4-8
	5.0% arom-carb	105	7-23
	0.5% arom-carb + 0.5% water	125	6-22
	2.0% arom-carb + 0.5% water	125	4-20
	5.0% arom-carb + 0.5% water	125	3-19

Remarks relating to Table F:

a) Pot-life of the coating mixture

The results show that:

- the reaction temperature can be increased by the 5 addition of an equivalent short measure of a polyketonediol. The effect is stronger when water is added too and most pronounced when both water and acid are added.
- the reaction temperature can be increased by the 10 addition of an acid, an amine- or an OH- functional compound, or an aliphatic or aromatic polycarbodiimide solution. When water is added as well, the effect is stronger.
- the pot-life is increased by the addition of a 15 polyketonediol, water and/or acid.

Example 10: Evaluation of the effect on the reaction temperature where a polyurethane coating is formed from a coating mixture and of the 20 effect of added solvents after the equilibration time of the mixture of a short measure of a polyisocyanate and a dispersion of a compound containing a reactive hydrogen.

25 The procedure of Example 5 was repeated, while in this example a short measure of HDI was added to the dispersion of CDH, prior to the preparation of the coating mixture. After the addition of HDI to the CDH-dispersion the mixtures were equilibrated for various periods of 30 time, before they were used in the coating mixture. The isocyanate-functional polyurethane of Example 3 was used in the tests. The results are presented in Table G. Further, CDH-dispersions and CDH-dispersions treated with HDI were mixed with a solvent and equilibrated for at 35 least 90 hrs and used according to the procedure of Example 5. The results are also presented in Table G.

Table G: the effect of the equilibration time of the mixture of a short measure of HDI and a dispersion of CDH on the reaction temperature of the formation of a polyurethane coating using a coating mixture and the

5 effect of the addition of solvents to the CDH-dispersion

Additive added to the CDH-dispersion	solvent added to the CDH-dispersion	equilibration time CDH-dispersion + HDI and/or solvent (hrs)	minimal temperature complete curing within 3 min (°C)	Pot-life at 50°C between ^{b)} (hrs)
--	--	--	90	0-0.8
0.02 SA HDI	--	0	90	0.5-0.8
0.02 SA HDI	--	0,2	95	20-168
0.02 SA HDI	--	1	100	20-168
0.02 SA HDI	--	16	110	168-240
0.02 SA HDI ^{a)}	--	16	120	168-240
0.02 SA HDI	--	90	125	168-240
0.02 SA HDI	--	360	125	168-240
0.02 SA HDI	--	432	125	168-240
--	2% isohexane	90	100	2-6
--	2% toluene	90	105	6-28
--	2% NMP	90	100	5-28
--	2% EtOAc	90	100	4-27
0.02 SA HDI	2% isohexane	90	125	>240
0.02 SA HDI	2% toluene	90	125	>240
0.02 SA HDI	2% NMP	90	130	3-70
0.02 SA HDI	2% EtOAc	90	125	>240
0.02 SA HDI	20% isohexane	90	125	>240
0.02 SA HDI	20% toluene	90	125	>144
0.02 SA HDI	20% NMP	90	110	3
0.02 SA HDI	20% EtOAc	90	130	43-136

remarks relating to Table G:

a) coating mixture after 74 hrs at 50°C, in which a CDH-dispersion with HDI is used which is equilibrated for 16 hrs

10 b) Pot-life of the coating mixture

The results show that:

- a higher reaction temperature can be obtained by

15 equilibrating the CDH-dispersion with HDI for a longer period.

- after a definite length of time of equilibration of the

- the pot-life of the coating mixture is lengthened by a longer equilibration period of the CDH-dispersion with HDI.
- the reaction temperature can be increased to some 5 extent by the addition of a solvent to the CDH-dispersion.
- when a CDH-dispersion with HDI to which also a solvent is added is used, the reaction temperature is comparable to the material without solvent. Only in the 10 presence of a larger amount of NMP the oligomer layer around the polyhydrazide dissolves or softens and the reaction temperature decreases again.

15 Example 11: Evaluation of the effect of the addition of water or acid to a coating mixture on the reaction temperature for the formation of a hydrazone coating.

PEC-205 was mixed with a, with respect to the ketone amount (1.87 meq/g), equivalent amount of a 4:6 by 20 weight dispersion of carbodihydrazide or adipic dihydrazide in polypropylene glycol with a molecular weight of 2000. Water and/or acid was added to the mixture. Further, the completely equilibrated CDH-dispersion with 0.02 SA HDI from Example 6 was mixed with 25 PEC-205. The mixtures were spread onto an infrared cell and the cell was placed for 2, 3, 5, 8, 12, 20, 40, 60 or 90 min at different temperatures. The time to complete the reaction was tested by infrared spectroscopy. When ADH was used the signal at 1630 cm^{-1} disappeared and a signal 30 appeared at 1740 cm^{-1} . When CDH was used the signal at 1637 cm^{-1} disappeared and a signal at 1740 cm^{-1} appeared. The results are presented in Table H.

Table H: Effect of water and acid on the coating formation using a polyketonediol and a carbodihydrazide dispersion or an adipic dihydrazide dispersion.

Compound containing a reactive hydrogen	additive added to the coating mixture	Reaction temperature (°C)	complete curing within (min)
ADH-dispersion	-	120	90
	2% water	120	60
	5% water	120	60
	-	140	60
	2% water	140	20
	5% water	140	20
	-	160	20
	2% water	160	8
	5% water	160	5
	2% (20% p-TSA in water)	160	3
	2% (20% p-TSA in DMM)	160	3
	-	190	8
	2% water	190	5
	5% water	190	5
CDH-dispersion	-	160	40
	2% water	160	40
	2% (20% p-TSA in water)	160	8

5

The results show that:

- A quicker reaction can be obtained by increasing the reaction temperature, and/or by the addition of water and/or an acid.

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Example 12: Evaluation of the effect on two-step reactions which are executed with the product of Example 4 after the addition of several additives to a dispersion of a compound containing a reactive hydrogen.

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50 g of the product of Example 4 was mixed with a, with respect to the NCO-amount, equivalent amount of a 4:6 (w/w) dispersion of CDH in Bisoflex TOT and with 1 g of a black pigment dispersion (obtainable as PermaQure GP-7715 from Stahl Holland). Beforehand several additives were added to the dispersion of CDH or to the coating mixture. The obtained mixtures were spread as 500 µm films

onto a pre-heated plate. The temperature was serially raised by of 5°C ($\pm 1^{\circ}\text{C}$) at a time. After 3 min the progress of the reactions was checked. The lowest temperature required to obtain a dry and flexible film was 5 measured. The results are presented in Table I. Next the films were embossed by pressing a pattern into them for 20 sec at 200°C and $6 \cdot 10^5 \text{ Pa}$ (6 atm). Thereafter the films were further cured by exposure to UV-radiation at 240 nm and a total energy amount of 4000 mJ/cm^2 . The embossed 10 films were placed for 24 hrs at 120°C to test the stability of the grain. The results are presented in Table I.

15 Table I: Effect of additives on the two-step reaction
executed with the product of Example 4.

added to the coating mixture	Added to the CDH-dispersion ^{a)}	minimal temperature complete curing	embossability of the films	films exposed to UV-radiation	grain stability at 120°C
-	-	90	good good good	no yes no	moderate good moderate
3% water	-	80	good	yes	good
-	0,05 SA HDI	120	good good good	no yes	moderate good
-	1% water	130	good good	no yes	moderate good

Remarks relating to Table I

20 - The CDH-dispersion with additives was equilibrated for 24 hrs at 50°C .

The results show that:

25 - the addition of water to the coating mixture allows the reaction temperature of the first reaction step to be decreased; which means the stage during which the film is formed.

- the addition of water or HDI to the CDH-dispersion may cause the reaction temperature of the first reaction step to be increased; which means the stage during which

the film is formed.

- the additives have no influence on the embossability.
- the stability of the grain in the films is much better when the films are exposed to UV-radiation in a second reaction step.

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Example 13: Evaluation of the two-step reaction between the product of Example 1 and a mixture of a CDH-dispersion and a CDH-dispersion which is treated with HDI.

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The isocyanate-functional polyurethane prepolymer of Example 1 was mixed with a CDH-dispersion in Bisoflex (4:6 w/w), a CDH dispersion which was treated with HDI and equilibrated for 95 hrs from Example 10, or a mixture of these two dispersions in a ratio of 0.5 : 0.5 SA. Films were spread onto a pre-heated plate and after 3 min the film was checked to see if it was still wet, tacky because of the formation of the film was not completed, or if the film formation was completed. The results are presented in Table J.

25

compound containing reactive hydrogen	phase of the film within 3 min at a temperature of		
	wet	tacky	cured film
1.0 SA CDH-dispersion	20-75	80- 85	90
1.0 SA (CDH-dispersion with 0.02 SA HDI)	20-90	95-105	110
0.5 SA CDH-dispersion + 0.5 SA (CDH-dispersion with 0.02 SA HDI)	20-85	90-105	110
0.8 SA CDH-dispersion + 0.2 SA (CDH-dispersion with 0.02 SA HDI)	20-80	85-100	105

The results show that

- the reaction temperature can be increased by the addition of HDI to the CDH-dispersion.

- when a mixture is used of the CDH-dispersion and a mixture of the CDH dispersion which was treated with HDI, a first reaction takes place at a lower temperature, so that the initial film is still tacky and 5 sticky and the second reaction takes place at a higher temperature.

10 Example 14: Evaluation of the two-step reaction between the product of example 3 and a mixture of a CDH dispersion and a CDH dispersion which was treated with HDI.

15 The isocyanate-functional polyurethane prepolymer of Example 3 was mixed with a CDH-dispersion in Bisoflex (4:6 w/w) and a CDH dispersion which was treated with HDI and equilibrated for 95 hrs from Example 10, in a ratio of 0.7: 0.3 equivalent. A film was spread onto a pre-heated plate at 100°C and after 3 min the film was removed. Subsequently the film was embossed by pressing a pattern in it for 20 sec at 200°C and 6.10^5 Pa (6 atm). The 20 embossed film was then heated for 24 hours at 120°C to check the stability of the grain. A film in which only the CDH-dispersion in Bisoflex was used as compound containing a reactive hydrogen was used as standard for comparison. The reactions were executed with or without water in the 25 coating mixture. The results are presented in Table K.

Table K: Results of the two-step reaction between the product of Example 3 and a mixture of a CDH-dispersion and a CDH dispersion which was treated with HDI.

5

Compound containing reactive hydrogen	Added additive to a coating mixture (weight %)	curing of the first reaction step (°C)	embossability of the films	grain stability at 120°C
1.0 SA CDH-dispersion	--	95	moderate	grain stays as it was
1.0 SA CDH-dispersion	3% water	80	moderate	grain stays as it was
0.7 SA CDH-dispersion + 0.3 SA(CDH-dispersion with 0.02 SA HDI)	--	95	good	good
0.7 SA CDH-dispersion + 0.3 SA(CDH-dispersion with 0.02 SA HDI)	3% water	80	good	good

The results show that:

- The films which were prepared with only the CDH-dispersion have reacted and crosslinked so far that they cannot be embossed anymore. This appeared to be the case for both the films with and without the addition of water to the coating mixture.
- For the films in which water was present in the coating mixture the reaction temperature of the first step can be decreased.
- The films, in which a part of the compound containing a reactive hydrogen is treated with HDI, are still embossable after the first reaction step and only cure completely during embossing at 200°C.